ATMOSPHERIC COMPOSITION

ORIGIN OF THE ATMOSPHERE:

The origin of our earth's atmosphere is still subject to much speculation. However, one theory seems fairly certain; that when the earth was formed some five billion years ago, it was probably too hot to retain any of the atmosphere it had to begin with. Based on our knowledge of gases in the universe, this first atmosphere probably consisted of helium, hydrogen, ammonia and methane.

If we assume that volcanoes five billion years ago emitted the same gasses as they do today, the earth's second atmosphere probably consisted of water vapor, carbon dioxide, and nitrogen. These gasses were expelled from the earth's interior by a process known as outgassing.

The vast amounts of water vapor expelled by the volcanic earth resulted in the formation of clouds which, in turn, produced rain. Over a period of thousands of years, the rain accumulated as rivers and lake and ocean basins.

EXPLORES! ASKS?
Why is some water considered "fresh water" and some water considered "salt water" and how might the differences have come about?

During this time, the water reservoirs acted as sinks for the large amounts of carbon dioxide (as they do today) and through chemical and biological processes became locked up in sedimentary rocks as limestone. The nitrogen, which is not very chemically active continued to accumulate in the atmosphere. In addition, evidence exists that the Sun was stronger several billion years ago, strong enough to radiatively split (called photodissociation) water vapor molecules into hydrogen and oxygen. The hydrogen, being very light, escaped into space, while the heavier oxygen accumulated in the atmosphere.

These processes acting sequentially and simultaneously appear to have produced the delicate balance of 78% nitrogen (N2) and 21% oxygen (O2) we observe today.

PRESENT COMPOSITION OF THE ATMOSPHERE:

The atmosphere is comprised of gases which are considered to be permanent (gases which remain essentially constant by percent) and gases considered to be variable (gases which have changing concentrations over a finite period of time).

PERMANENT gases in the atmosphere by percent are:

        Nitrogen   78.1%
        Oxygen   20.9%

(Note that these two permanent gases together comprise 99% of the

Other permanent gases:

        Argon   0.9%
        Neon   0.002%
        Helium   0.0005%
        Krypton   0.0001%
        Hydrogen   0.00005%

VARIABLE gases in the atmosphere and typical percentage values are

        Water vapor   0 to 4%
        Carbon Dioxide   0.035%
        Methane   0.0002%
        Ozone   0.000004%

Return to the Skills and Activities menu

composition of pure air (in atmospheric chemistry)

The composition of air is variable with respect to several of its components (e.g. CH_4, CO_2, H_2O) so 'pure' air has no precise meaning; it is commonly considered to be air which is free of dust, aerosols and reactive gaseous contaminants of anthropogenic origin. The composition of the major components in dry air is relatively constant (percent by volume given): nitrogen, 78.084; oxygen, 20.946; argon, 0.934; carbon dioxide, 0.033; neon, 0.0018; helium, 0.000524; methane, 0.00016; krypton, 0.000114; hydrogen 0.00005; nitrous oxide, 0.00003; xenon, 0.0000087. The concentrations of carbon dioxide, methane, nitrous oxide, the chlorofluorocarbons and some other species of anthropogenic origin are increasing measurably with time. Relative clean air which is free of most reactive anthropogenic pollution (NO, NO_2, SO_2, non-methane hydrocarbons, etc.), often used as a reference sample in the calibration and operation of instruments, is purchased under the designation of zero air.

1990, *62*, 2172

Chemical of the Week

GASES OF THE AIR

The air around us is a mixture of gases, mainly nitrogen and oxygen, but containing much smaller amounts of water vapor, argon, and carbon dioxide, and very small amounts of other gases. Air also contains suspended dust, spores, and bacteria. Because of the action of wind, the percent composition of air varies only slightly with altitude and location. The table indicates the composition of a typical sample of air after all water vapor and suspended particles have been removed.

The amount of water in the air varies tremendously with location, temperature, and time. In deserts and at low temperatures, the content of water vapor can be less than 0.1% by volume. In warm, humid zones, the air may contain over 6% water vapor.

Air is the commercial source for many of the gases it contains. It is separated into its components by fractional distillation of liquefied air. Before air is liquefied, water vapor and carbon dioxide are removed, because these substances solidify when cooled and

Composition of Dry Air	
Substance	% by volume
Nitrogen, N_2	78.08
Oxygen, O_2	20.95
Argon, Ar	0.93
Carbon dioxide, CO_2	0.033
Neon, Ne	0.0018
Helium, He	0.00052
Methane, CH_4	0.0002
Krypton, Kr	0.00011
Nitrogen(I) oxide, N_2O	0.00005
Hydrogen, H_2	0.00005

would clog the pipes of the air liquefaction plant. The dry, CO_2-free air is compressed to about 200 atmospheres. This compression causes the air to become warm, and the heat is removed by passing the compressed air through radiators. The cooled, compressed air is then allowed to expand rapidly. The rapid expansion causes the air to become cold, so cold that some of it condenses. By the alternate compressing and expanding of air, most of it can be liquefied.

Nitrogen is obtained from liquid air by distillation at -196°C. The gas obtained by this process is actually a mixture of nitrogen and about 1.25% noble (or "inert") gases, argon, neon, krypton, and xenon. Nitrogen is second only to sulfuric acid in the volume produced by the U.S. chemical industry. Its major uses are as an inert blanketing atmosphere in chemical processing (14%), electronics (15%), and, in liquid form, as a freezing agent (21%). Nitrogen is used to make agricultural fertilizers, such as ammonia and nitrates. It is also used in the production of acrylonitrile, CH_2=CHCN, which is important in the manufacture of synthetic fibers such as Orlon, and in the production of cyanamide, HN=C=NH, which is polymerized to Melamine plastic. Because it is a very poor oxidizing agent, nitrogen is used to pack oxidizable foods, such as ground coffee, and as an inert atmosphere in the manufacture of electronic components. Liquefied nitrogen, because it is

very cold, is used extensively to chill materials for preservation, as in freeze-drying of foods, and in manufacturing processes that require low temperatures, such as machining of aluminum.

The lighter noble gas neon is obtained from air. Its boiling point (-246°C) is too low for neon to condense during the liquefaction of air, and neon concentrates in the gas that remains after air is liquefied. (This remaining gas also contains helium, but the major commercial source of helium is natural gas, in which its concentration is much higher than it is in air.) The heavier noble gases argon, krypton, and xenon are obtained by the fractional distillation of liquid air. Under the proper conditions, a fraction containing roughly 60% noble gases, 30% oxygen, and 10% nitrogen can be obtained from liquid air. Oxygen is removed from the mixture by passing it over hot copper. Oxygen reacts with hot copper to form copper(II) oxide, CuO. The remaining gas is a mixture of noble gases and nitrogen. This mixture is the gas used to fill incandescent light bulbs. Nitrogen is removed from the mixture by passing the mixture over hot magnesium, which reacts with nitrogen to form magnesium nitride, Mg_3N_2. The remaining gas is a mixture of argon, neon, krypton, and xenon. Because these elements are chemically very unreactive, chemical means cannot be used to separate them. They are separated by adsorbing the liquid mixture onto activated charcoal at very low temperature. As the activated charcoal is warmed slowly, each gas desorbs individually in a particular temperature range. When the temperature is raised to -80°C, the gas that escapes is nearly pure argon. As the temperature is raised to higher temperatures, nearly pure krypton, and then xenon, are released.

Argon is the most abundant and most used of the noble gases. Its chief uses are in metallurgy, where it provides an inert atmosphere in which hot metals can be worked. Because argon is so very unreactive, it prevents chemical reactions of the very hot metal being welded or forged. Perhaps the most familiar use of the noble gases is in "neon" signs. These are lamps constructed usually from clear, colorless glass tubes filled with a gas which emits light when an electric current passes through it. Pure neon in such a tube produces orange-red light, argon produces blue-green. (Other gases are also used; for example, mercury vapor produces blue light. Other colors are produced by using colored tubes, mixtures of gases, and fluorescent coatings inside the tubes.)
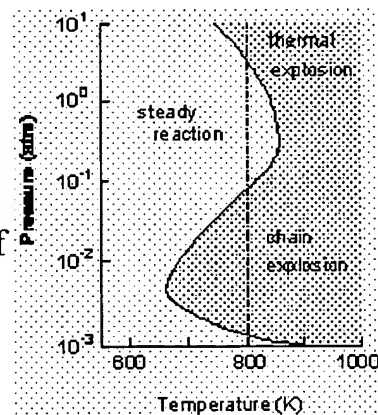
Nearly all commercial oxygen (over 95%) is produced by fractional distillation of liquid air. It boils at -183°C. Oxygen is the third highest-volume chemical produced in the U.S., and most of this product is more than 99.5% pure. Oxygen is paramagnetic, that is, it is attracted to a magnet. Liquid oxygen is pale blue. The major commercial uses of oxygen are in metal manufacturing (30%), metal fabricating (33%), and in health services (13%). In the steel industry, oxygen is passed through impure molten iron in a blast furnace to oxidize and remove impurities such as carbon, sulfur, phosphorus, and silicon. Oxygen is also used as the oxidant in torch cutting of steel. In this process, the steel is heated by an oxygen-acetylene flame, and a stream of hot oxygen is directed at the hot steel. The hot

steel is oxidized by the hot oxygen and erodes away, severing the steel. Oxygen is also used extensively in the chemical industry, such as in the production of nitric acid, HNO_3, from ammonia, NH_3.

The reaction of oxygen with another gas can lead to an explosion. There are two reasons why a reaction results in an explosion, and therefore, two types of explosions. *Thermal explosions* result from temperature effects on the rate of a reaction. *Chain reaction explosions* result from the behavior of the reacting molecules.

In a thermal explosion, the heat released by the reaction increases the temperature of the reacting mixture. This increased temperature increases the rate of the reaction. If heat released by the reaction cannot escape, the rate of the reaction increases rapidly, and an explosion can result. Heat is likely to build up in a reacting gas mixture when the pressure is high, because under these conditions, individual "hot" molecules cannot move very far and the energy is contained. Thus, thermal explosions are likely to occur at high pressures.
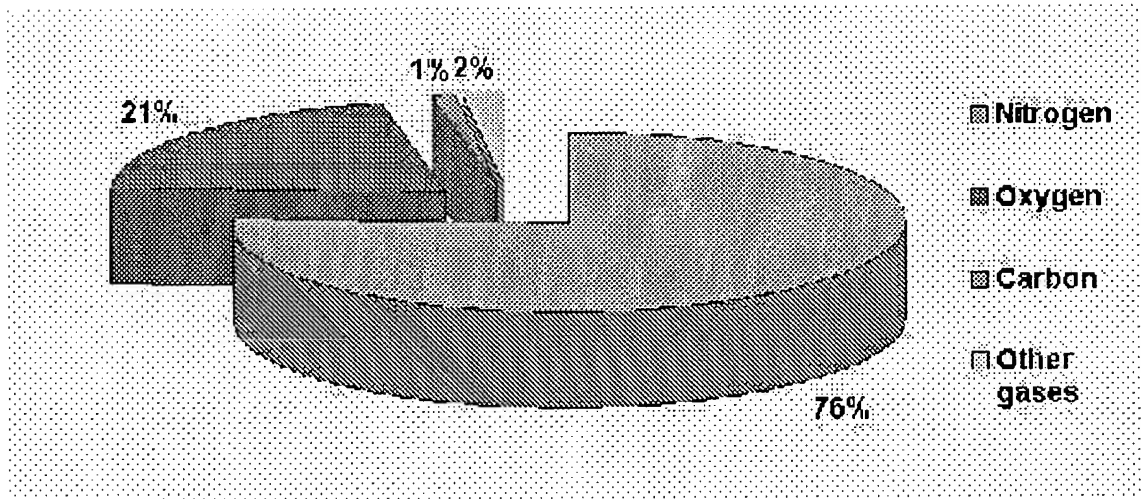
In a chain reaction explosion, the reaction occurs in such a way that the number of highly reactive particles (called free radicals) increases during the reaction. The reaction of hydrogen and oxygen occurs in such a fashion. If the pressure is very low, free radicals are likely to collide with the walls of the container before reacting with other molecules, and no explosion occurs. If the pressure is high, the free radicals are likely to collide with each other, terminating a reaction chain, and no explosion occurs. Only when free radicals collide with molecules and generate other free radicals does the chain reaction continue, producing an explosion. Thus, chain reaction explosions are likely to occur at intermediate pressures.
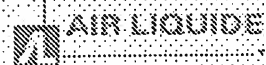
The figure shows how the explosiveness of a hydrogen-oxygen mixture depends on temperature and pressure. Explosion occurs in the shaded area. At 800K and low pressure, no explosion occurs. As the pressure is raised, the mixture enters the chain reaction explosion region. As the pressure is raised further, the mixture is no longer explosive. When the pressure is increased even more, the mixture enters the thermal explosion region.

Back to Chemical of the Week.

The Composition of Air

Nitrogen

Oxygen

Carbon

Other gases

21%

1% 2%

76%

Oil & Gas

Applications

SRU Oxygen Enrichment

Technologies using oxygen to expand the capacity of Claus Sulfur Recovery Units (SRU) or to build peak shaving process capability into new units are now widespread in the refining industry. Oxygen use in SRUs provides more than just capacity advantages, it can increase the combustion efficiency of the furnace and in some cases the overall sulfur recovery efficiency of the sulfur facility. If the refinery processes ammonia bearing sour water stripper gas, SRU's are often faced with ammonium salt formation and pluggage by these salts in heat exchange equipment. The use of oxygen can help promote the destruction of ammonia and ensure that ammonium salt formation is minimized. Oxygen can also help in the combustion of lean acid gas feeds.
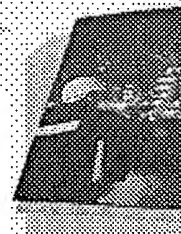
• Oxygen enrichment to 28 % volume

Oxygen enrichment involves blending an oxygen rich stream into a combustion air line to increase the air stream up to a maximum of 28 % volume. The system is quite inexpensive, usually requiring oxygen supply equipment, a control skid, a sparger (AIR LIQUIDE's OXYNATOR™), and associated piping. Enrichment can typically be implemented without any modifications to the existing burner. The capacity increase that can be achieved through oxygen enrichment ranges from 25 to 30 %. Oxygen enrichment can be applied in virtually any SRU. Our references indicate that no modifications are required downstream of the furnace. If expansion of over 30 % is required, you should consider making a detailed analysis of all equipment in the sulfur and tailgas units. At AIR LIQUIDE, we work with qualified engineering firms to implement such projects.

With oxygen enrichment, installation can occur without any interruption to the operation of the SRU. The air line can be hot-tapped between turnarounds or cold-tapped in a previous turnaround. The Oxynator™ can be installed at any time through a full port valve that has been sized for the apparatus. An oxygen flow control skid and supply system can be installed prior to any process changes to the unit. Once all the equipment is in place, oxygen can be introduced into the SRU to improve its performance.

• Oxygen enrichment greater than 28 % volume and ammonia destruction

At AIR LIQUIDE, we have developed a unique burner (Oxyburner™) to help refiners to completely destroy ammonia in feeds to SRU's. This burner allows greater than 28 % oxygen enrichment, up to 100 % concentration to increase SRU capacity, ensure ammonia destruction with a turndown of 7:1 on air. The burner can easily retrofit existing SRU furnaces.

Taiwan Thaila
United King
U.S.A.

Oil & Gas

Applications

SRU Oxygen Enrichment

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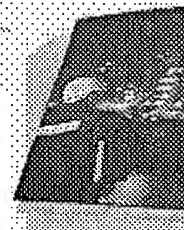
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Taiwan Thaila
United King
U.S.A.

Composition of Air

Mainly Oxygen and Nitrogen

More Nitrogen than Oxygen plus small amounts of other stuff

Nitrogen	Oxygen	Other Stuff
4/5	1/5	Not much
78%	21%	1%

Composition of Dry, Unpolluted Air (by volume)

Constituent	percent	Constituent	parts per million
Nitrogen	78.084 ± 0.004	Neon	18.18 ± 0.04
Oxygen	20.946 ± 0.002	Helium	5.24 ± 0.004
Argon	0.934 ± 0.001	Methane	2
Carbon Dioxide	0.033 ± 0.001	Krypton	1.14 ± 0.01
		Hydrogen	0.5
		Dinitrogen Oxide	0.5 ± 0.1
		Xenon	0.087 ± 0.001

Handbook of Chemistry and Physics, 57th Ed (1076), p. F210

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Material Properties - Material properties as densities, heat capacities for gases, fluids and solids ....

Composition of Air

Dry air is a mechanical mixture of several gases.

Air is a mixture of gases, 78% nitrogen and 21% oxygen with traces of water vapour, carbon dioxide, argon, and various components. We usually model air as a uniform (no variation or fluctuation) gas with properties that are averaged from al individual components.

Gas	Dry air %	
	By volume	By weight
Oxygen	20,99	23,20
Nitrogen	78,03	75,47
Carbon dioxide	0,03	0,046
Hydrogen	0,00005	~ 0
Argon	0,93	1,28
Neon	0,0018	0,0012
Helium	0,0005	0,00007
Krypton	0,0001	0,0003
Xenon	$9 \cdot 10^{-6}$	0,00004

The composition of air is unchanged until the height of approximately 10.000 m.

The average air temperature diminishes at the rate of about $0,6^{\circ}$C for each 100 m vertical height

"One Standard Atmosphere" is defined as the pressure equivalent to that exerted by a 760 mm column of mercury at 0°C and at standard gravity (32.174 ft/sec^2).

Equivalents to one atmosphere

- 76 Centimetres (760 mm) of Mercury
- 29.921 Inches of Mercury
- 10.332 Meters of Water
- 406.78 Inches of Water
- 33.899 Feet of Water
- 14.696 Pound-Force per Square Inch
- 2116.2 Pounds-Force per Square Foot

- 1.033 Kilograms-Force per Square Centimetre
- 101.33 Kilopascal

More about Temperature, Density, Specific heat, Thermal Conductivity - the properties of air.

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Composition of Air

Gas	% of Earth Atmosphere at sea level (dry air)
Nitrogen	78.08
Oxygen	20.95
Argon	0.93
Carbon dioxide	0.03
Neon	0.0018
Helium	0.0005
Krypton	0.0001
Xenon	0.00001

Composition of Air
78.08% N_2
20.95% O_2
0.93% Ar
0.03% CO_2
0.002% Ne
Plus lesser amounts of Methane, Helium, Krypton, Hydrogen, Xenon

Gasses Playing Important Biological Roles
O_2
CO_2
N_2

Solubility of Biol. Important Gasses in Water
Although it is less common in air than nitrogen, oxygen is more soluble in water
Solubilities at 10C:

	At 1 atm:	At normal partial press.	
N_2	18.61		14.53
O_2	37.78		7.90
Ar	41.82		0.39
CO_2	1194		0.39

Other Important Gasses in Natural Waters
CH_4 (methane) from anaerobic decay and atmospheric imputs
NH_3 (ammonia) Bacterial decomposition and excretion of organisms
H_2S (hydrogen sulfide) anaerobic decomposition, no atmospheric inputs

Factors Affecting the Solubility of Gasses in Natural Waters

Partial pressure (p) ▬ How much gas is available vs. total gasses in atmosphere

Temperature (T)- gas solubility decreases with increased T.

Salinity ▬ gas solubility decreases with increased salinity. For example, oxygen saturation is 20% less in sea water vs. fresh water.
Chemical Nature of the Gas (polarity, molecular size, reactivity)

Henry's Law
At constant temperature:

c (conc.) = K (solu. Constant) x p (partial pressure

Saturation Level
The maximum concentration (usually in mg/L or ppm) of a gas that can remain dissolved in water at a specific temperature and pressure. It is possible for gasses to become temporarily supersaturated in waters due to rapid inputs and/or changing temperatures. Supersaturation can be a serious problem for aquatic organisms, causing bubble formation in tissues and capillaries. Even bubbles of oxygen can clog gill capillaries, causing suffocation.

Altitude Effects on Solubility
Increased altitude decreases the partial pressure of a gas, therefore decreasing solubility (think of carbonated beverages). On average, solubility decreases 1.4% with each 100m increase in altitude. More specifically:

0 – 600m a 4% decrease/300m increase in altitude
600 – 1500m a 3% decrease/300m increase in altitude

1500 – 3050m a 2.5% decrease/300m increase in altitude

Diffusion of Gasses into Water
In stagnant waters, oxygen (or any gas) diffusion is very slow because the waters surface tension needs to be overcome
However, under wind and wave conditions, the resistance of the surface tension is overcome and waves tend to incorporate gas bubbles. Therefore, diffusion into the water column is greatly increased.

O_2 Concentration in Natural Waters
O_2 Concentration =
(Atmospheric diffusion + Surface (rivers) Inputs) -
(Evasion to Atmosphere + Dark rx. of Photosynthesis (plant respiration) + Bacterial respiration (aerobic respiration) + Animal respiration + chemical oxidation)

Oxygen-Depth Profiles During Thermal Stratification
Orthograde Profile - seen during turnover and in oligotrophic, stratified lakes with little production of organic matter
Clinograde Profile - seen in highly productive eutrophic lakes, profile extreme in meromictic lakes
Positive Heterograde Profile - Oxygen conc. Peaks in the metalimnion. Sometimes 400% saturation reached. Due to algae that thrive under lower light condits., or sinking, live algae. This usually seen with

buried Chlorophyll maxima.
Negative Heterograde Profile - Oxygen conc. Has a minima in metalimnion which increases before hypolimnion. This caused by many respiring zooplankters in metalimnion or decaying matter trapped by density gradients.
Note: Lakes can show one or more of these profiles throughout the year.

Horizontal Variations in Oxygen Concentration
Horizontal variations in oxygen concentration are usually small during spring and fall turnover. During the summer and when the lake is under ice cover, the O2 concentration of the littoral zone is very different than that in the open water. Oxygen conc.in the littoral zone also fluctuates widely on a daily basis. This is due to the larger quantities of macrophytes photosynthesizing during the day and oxygen consuming bacterial respiration occurring at the sediment-water interface at night. Additional littoral zone fluctuations, both horizontal and vertical can occur due to some macrophytes actively photosynthesizing while others die off, respire, or go dormant.

Oxygen Deficit

Deficit = Saturation Value - Actual Value
Actual Oxygen Deficit is defined as the difference between the saturation value and the actual value of dissolved oxygen at a specific temperature, salinity, and pressure.
Absolute oxygen deficit is this difference at 4C

Relative Areal Hypolimnetic Oxygen Deficit
This is defined as the volumetric loss of oxygen from the hypolimnion during summer stratification. This is used by limnologists as a relative measure of primary productivity. The assumption is that the amount of aerobic decomposition in the hypolimnion or tropholytic decomposition is equivalent to the amount of photosynthesis or trophogenic production and assumes little loading of allochthanous organic matter.

Summerkill
The oxygen concentration in the littoral zone may be extremely reduced. This usually occurs in highly productive lakes with a relatively large area of littoral zone with extensive macrophyte growth. At the end

of summer, many of these plants die and the resulting decomposition may severely deplete dissolved oxygen levels even into the epilimnion. Often entire fish populations are lost during this summerkill.

Winterkill
During periods of thick snow and ice cover, a lake may be in total darkness. Highly productive (eutrophic) lakes suffer massive die-off of algae and macrophytes. The resulting decomposition severely depletes available oxygen resulting in winterkill. Methane and hydrogen bubbling up from anaerobic sediments in these lakes may become oxidized (react with oxygen in the water column), also depleting oxygen concentrations.

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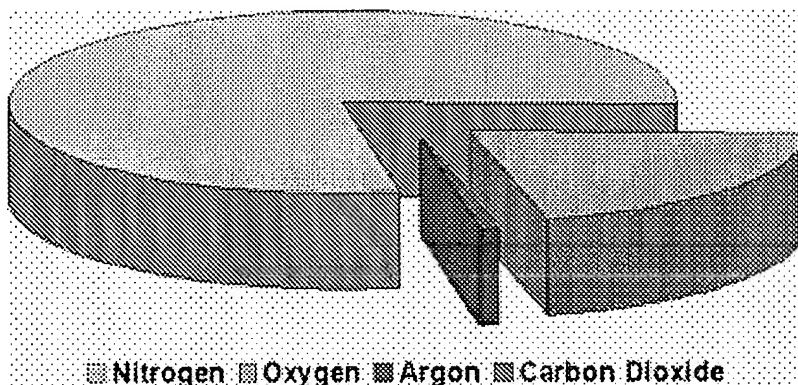**The Online Knowledge Magazine**

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Composition of Air

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■ Nitrogen ▨ Oxygen ■ Argon ▨ Carbon Dioxide

Human Respiration
The air that leaves a person's lungs during exhalation contains 14% oxygen and 4.4% carbon dioxide.

Atmospheres with oxygen concentrations below 19.5 percent can have adverse physiological effects, and atmospheres with less than 16 percent oxygen can become life threatening.

Component	Symbol	Content	
Nitrogen	N_2	78.084%	
Oxygen	O_2	20.947%	99.998%
Argon	Ar	0.934%	
Carbon Dioxide	CO_2	0.033%	
Neon	Ne	18.2 parts per million	
Helium	He	5.2 parts per million	
Krypton	Kr	1.1 parts per million	
Sulfur dioxide	SO_2	1.0 parts per million	
Methane	CH_4	2.0 parts per million	
Hydrogen	H_2	0.5 parts per million	
Nitrous Oxide	N_2O	0.5 parts per million	
Xenon	Xe	0.09 parts per million	
Ozone	O_3	0.07 parts per million	
Nitrogen dioxide	NO_2	0.02 parts per million	
Iodine	I_2	0.01 parts per million	
Carbon monoxide	CO	trace	

| Carbon monoxide | CO | trace |
| Ammonia | NH_3 | trace |

Concentration of Oxygen in the Air

This is an attempt to use a microscale method to measure the concentration of oxygen in air. The method is still not perfected. I would welcome feedback from anyone who would like to try out the method: how successful do you find it? Do you find it consistent? What difficulties do you find? Any suggestions for improvement? Comments and suggestions to Mike Clark,

For monitoring of the temperature of the experiment, I have been using a CBL temperature probe rather than a cheaper digital thermometer or a liquid-in-glass thermometer.

PROPORTION OF OXYGEN IN AIR

AIM To measure the proportion of oxygen, by volume, in a sample of air.

-

MATERIALS REQUIRED One graduated 1 mL pipette, pipette filler bulb, digital thermometer to read to 0.1 degrees C, watch or clock, retort stand with clamp, about 0.6 mL of 1.0M solution (1.9 g dissolved in 10 mL of solution) of sodium pyrosulfite, $Na_2S_2O_5$, (also known as sodium metabisulfite).

PREDICTIONS AND PLANNING

Some chemical substances in aqueous solution react with oxygen gas quite readily. Examples include sulfites, iron(II) ions and tin(II) ions. If such a substance were used to remove all the oxygen from a measured volume of air, then the loss of volume of the sample would indicate the proportion of oxygen in the sample.

A volume of air of about 0.7 mL can be held as a bubble in a horizontal 1 mL graduated pipette between two volumes of solution that can absorb oxygen. The volume of the bubble can be read to 0.001 mL (one tenth of a graduation). If the pipette is left for a length of time sufficient that no further change occurs in the volume of the bubble, then loss in the bubbleís volume should represent the volume of oxygen that was absorbed.

What solution should be chosen to absorb the oxygen? Sodium pyrosulfite produces fairly consistent results within a reasonable length of time. Solutions of tin(II) ions are difficult to prepare; they absorb oxygen well when the oxygen concentration of the air is high, but tend to react slowly and unreliably as the concentration of oxygen becomes low. Iron(II) sulfate solutions react slowly at low pH, and at higher pH they may leave rusty deposits in glassware.

A large excess of sodium pyrosulfite should be used. Oxygen is being absorbed at the air-liquid interfaces, the two menisci. A large excess of solute should reduce the slowing of the reaction caused by depletion of pyrosulfite reagent and accumulation of reaction products at the interfaces. Assuming a bubble size of 0.700 mL, then the content of oxygen should be a little over 0.140 mL, which represents approx 6 micromoles of oxygen gas. This amount would be absorbed by the same amount of pyrosulfite ions. This amount would be contained by about 6 microlitres of 1.0M solution. About 0.60 mL of 1.0M sodium pyrosulfite represents, therefore, an excess of approximately one hundredfold.

The volume of a gas changes with temperature, so it is necessary that temperature be recorded as well as volume. It will be assumed that the temperature of air in the bubble is the same as the temperature of surrounding air. The recorded gas volumes can be corrected for temperature, so that the initial and final volumes of gas in the bubble will be at equal temperatures. A thermometer that can read to 0.1 degrees C should be used.

The reactions involved are slow, so preparations should be made to gather observations over an extended period of time.

INSTRUCTIONS

Using a filler bulb, carefully draw sodium pyrosulfite solution into the one millilitre graduated pipette, up to about the 0.70 to 0.65 mL graduation.

Withdraw the pipette from the sodium pyrosulfite solution, and draw in about 0.7 mL of air. Draw in a further volume of 0.25 to 0.3 mL of solution, so that there is a clear bubble of air trapped between two volumes of solution, and the two menisci at the ends of the bubble lie both within the range of the graduations.

Hold the pipette vertically for about a minute to allow any film of liquid around the bubble to run down. Then holding the pipette in a horizontal position, work quickly to remove the filler bulb, and tilt the pipette slightly and gently so that solution runs into the tip without dripping out. Clamp the pipette with the tip tilted downwards at a very small angle, and promptly read the positions of the two menisci to the nearest tenth of a graduation, that is, to 0.001 mL.

Record the time, and the room temperature to 0.1 degrees C.

The pipette should be monitored for about forty-eight hours: the positions of the meniscus and the volume of the bubble should be recorded periodically. As the rate of shrinkage of the bubble slows down, the temperature should also be recorded. This must continue until the volume of the bubble ceases to shrink.

The volume of the bubble may vary as the room temperature changes. Towards the end of the reaction, if the temperature changes between two readings, it will be necessary to correct the volumes read to the initial temperature of the experiment, using the Charlesí Law equation.

During the reaction, if a small volume of solution flows down into the space occupied by the bubble of air, the pipette should be rocked carefully before a volume is read, allowing the liquid in the pipette to move slowly to and fro until the liquid is swept up, and the gas space is free of droplets of solution. During this process, the bubble must remain intact and no solution may be spilt from the pipette.

OBSERVATIONS

Records should be kept of the following observations:

**At each observation: time of observation, the positions of the menisci and thus the volume of the bubble.

**At setting-up, and at observations made towards the end of the reaction time: temperature.

ALL VALUES SHOULD BE RECORDED TO THREE SIGNIFICANT FIGURES:

The "volume of bubble" is the difference between the values at the two menisci bounding the air bubble. All pipette readings should have three digits: for example, a reading that is exactly 0.71 should be recorded as 0.710, while a reading that is exactly 0.1 should be recorded as 0.100.

Temperatures should also be recorded to the nearest 0.1°C, so a reading that is exactly 18°C should be recorded as 18.0°C.

As the reaction approaches its end, values for the "volume of bubble" is the volume of the bubble should be corrected to the initial temperature of the experiment, using the Charlesí Law equation.

The "volume of oxygen absorbed" is the difference between the initial volume of the air bubble and the corrected final volume of the bubble.

It may be observed that the rate of shrinkage of the bubble is quite rapid at first, but becomes slow after twelve to fifteen hours, as the partial pressure of oxygen drops.

INTERPRETATIONS AND EVALUATION

The percentage of oxygen in the sample can be calculated from the volume of oxygen absorbed compared with the initial volume of the bubble.

The final estimate of oxygen percentage in the air should be presented, therefore, to one decimal place, as, for example, 21.2%, or 21.0%.

EVALUATION OF ERRORS

There are some sources of error in this measurement:

**an error of 0.001mL in estimating the position of meniscus may have a small effect on final estimates of oxygen percentage.

**errors of as little as ±0.1°C in reading temperature may also affect volume readings, and therefore estimates of oxygen percentage.

**it is assumed in this procedure that oxygen is the only component of air that can vary and so affect the volume of the bubble. No account is taken of the water-vapour content of the initial air sample or of the final bubble, nor of the small partial pressure of sulfur dioxide in the airspace over the pyrosulfite solution.

**accuracy of results may be affected slightly by changes in atmospheric pressure over the time of the experiment.

This procedure should still be able to yield a proportion of oxygen in an air sample of between 20.0% and 22.0%. If the procedure is replicated several times, an average estimate could be made for percentage oxygen content of air.

Questions? Comments?

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